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## **TRIPLET EXCIMER FORMATION IN A PLATINUM ACETYLIDE (PREPRINT)**

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**APRIL 2007**

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# Triplet Excimer Formation in a Platinum Acetylide

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**Abstract**

To prove the source of ground state self-quenching in *trans*-Pt(P(C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>C≡CC<sub>6</sub>H<sub>5</sub>)<sub>2</sub> is a result of triplet excimer formation, we carried out nanosecond transient absorption measurements on multiple concentrations. By constructing a kinetic model for the system we were able to determine rate constants for the formation and decay of the triplet excimer,  $4.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  and  $6.9 \times 10^5 \text{ s}^{-1}$  respectively. We determined the transient absorption spectrum for the excimer which has an extinction coefficient maximum per excimer unit of  $95,680 \text{ M}^{-1}\text{cm}^{-1}$  at 600nm. Experimental analysis suggests that the formation of the triplet excimer is largely due to a ligand to ligand interaction.



## Introduction

Platinum acetylides are exceptional systems for investigating triplet state phenomena like ground state absorption to the triplet state, intersystem crossing, the triplet state absorption spectrum and phosphorescence(1-9). In our laboratory, we have been investigating the relationship between chemical structure and spectroscopic properties in platinum acetylide complexes(1,10,11). We recently synthesized a platinum acetylide  $\text{Pt}(\text{P}(\text{C}_8\text{H}_{17})_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$ , designated as PE2-octyl in Figure 1, that is a liquid at room temperature(8). The chromophore concentration is approximately 0.9 moles of chromophore per liter of liquid. Its high solubility and liquid character make it possible to investigate the photophysics from a dilute solution to a neat liquid. The triplet state of degassed, dilute PE2-octyl shows single exponential decay with a lifetime of 83  $\mu\text{s}$ , in good agreement with the 42  $\mu\text{s}$  lifetime of degassed, dilute PE2-butyl(1). The triplet state of air-saturated, neat PE2-octyl shows biexponential decay with a fast lifetime of 26 ns and a slow lifetime of 1.2  $\mu\text{s}$ . The different behavior in the neat liquid may result from a combination of oxygen quenching, triplet-triplet annihilation and triplet excimer formation.

In this paper we have investigated the behavior of the triplet state absorption spectrum of PE2-octyl as a function of concentration. We have found evidence of self-quenching resulting from formation of a triplet excimer and determined the triplet state absorption spectrum of the excimer. In contrast to the broad and featureless spectrum of the monomer unit, we found the excimer absorption spectrum to have a narrow band shape and vibronic structure.



## Experimental

Ground state UV/Vis absorption spectra were measured using a Cary 500 spectrophotometer. Nanosecond transient absorption measurements were carried out using a Q-switched Nd:YAG laser (Quantel Brilliant, pulse width ca. 5 ns). For self-quenching measurements, an optical parametric oscillator (OPO) was used to produce excitation wavelengths tunable from 320nm-470nm. The excitation wavelength was tuned with the OPO to match an optical density of  $<0.2$  in the sample. Pump fluences did not exceed  $8\text{mJ/cm}^2$ . A detailed description of the laser flash photolysis apparatus has been published earlier(1). All samples were prepared in benzene and deoxygenated by three cycles of freeze-pump-thaw.

The molar extinction coefficient of  $T_1 \rightarrow T_n$  absorption and the triplet state quantum yield was determined using the method of total depletion(12) and confirmed with singlet depletion, which has been described previously(1).

PE2-octyl was prepared as previously described(8).

## Results and Discussion

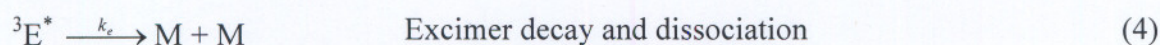
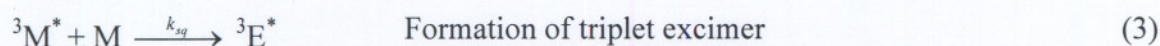
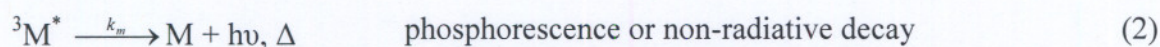
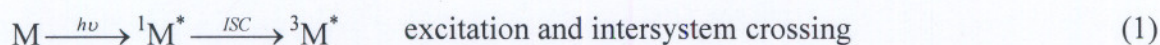
Typically, triplet excimers are observed through red shifted phosphorescence that has a characteristic rise that corresponds to the decay of the monomer followed by the excimer decay itself(13) or through transient absorption of the excimer with similar kinetic behavior(14). There has been a considerable amount of research on the excimer emission of bidentate substituted Pt (II) complexes with observable excimer emission(15-17). There has been little however on the self-quenching and excimer formation of *trans*-platinum poly-ynes(18). We have been able to detect triplet excimer formation in PE2-octyl by way of transient absorption. However, efforts to measure the emission from the



triplet excimer have been unsuccessful as the decay is likely non-radiative and therefore we have been unable to determine the energy separation between the triplet monomer and triplet excimer.

The first indication of a triplet excimer is found in Figure 3 which shows the transient absorption spectra for PE2-octyl at 57mM concentration in deoxygenated benzene as a function of time. At time zero, the spectrum resembles that of dilute (<10 $\mu$ M) PE2-octyl with a broad, featureless transition centered on 600nm. As time increases, the spectrum, which is still centered at 600nm, narrows and develops more vibronic structure which is likely due to a decrease in conformational mobility within the ligand in the excimer. This implies that the excimer structure is such that rotation along the acetylide axis is hindered. There is an isosbestic point located at 615nm suggesting that there are only two species present in the transient absorption spectra. This behavior is not present at dilute concentrations nor is there any evidence of ground state aggregation. Ground state Beer-Lambert plots are linear over the range tested in this study. While some triplet excimers have shown a red shift in the  $T_1 \rightarrow T_n$  absorption spectrum(14,19,20), however in this case the energy separation for the transition is conserved.

We use the following scheme to describe the reaction behavior for PE2-octyl monomer and excimer(21).





Here  $k_m$  and  $k_{sq}$  convolve to form one observed decay rate,  $k_{obs}$ , for the triplet monomer which is linear with ground state concentration  $[M]$ .

$$k_{obs} = k_m + k_{sq}[M] \quad (5)$$

Following integration of the differential equation for the change in triplet monomer concentration with time yields a first order exponential decay.

$$[{}^3M^*] = [{}^3M^*]_0 e^{-k_{obs}t} \quad (6)$$

Values for  $k_{sq}$  and  $k_m$  can be solved simply by a linear fit of  $k_{obs}$  versus concentration plot. A series of concentrations ranging from 1-10mM were deoxygenated, and their transient absorption spectra recorded for this purpose. Fig. 2 shows an example of the Stern-Volmer plot at 470nm. Because the spectral features for the triplet excimer and monomer overlap significantly, wavelengths must be chosen such that the differential absorbance decay is a result of only monomer excited states. For PE2-octyl, the wavelength range was set at 420-510 nm with the blue cutoff due to strong inter-filter effects and the red cutoff due to strong excimer absorption in the transient decay. Stern-Volmer plots at 10nm increments from 420-510nm were averaged to give a value for  $k_{sq}$  and  $k_m$  of  $4.7 \times 10^6 \pm 0.3 \text{ M}^{-1}\text{s}^{-1}$  and  $1.1 \times 10^4 \pm 0.2 \text{ s}^{-1}$  respectively. The order of magnitude agrees well with  $k_{sq}$  values reported for aromatic hydrocarbons(21) and  $k_m$  agrees well with measurements from dilute PE2-octyl(8). This does not however agree with values reported for Pt (II) diimine complexes where  $k_{sq}$  is on the order of  $10^9 \text{ M}^{-1}\text{s}^{-1}$  and has been described as a metal-metal interaction(15). Prior work has shown that the triplet state for the monomer PE2-octyl is localized on one of the conjugated ligands(22,23). Therefore, it seems likely that the formation of the triplet excimer is due largely to ligand



interactions for these molecules and seems to be reflected in the self-quenching rate constants resembling aromatic hydrocarbons. This was verified by quenching the triplet state of a similar compound PE2-ethyl,  $\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5)_2$ , with increasing concentrations of ligand,  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_5$ . The  $k_q$  was determined to be on the order of  $1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$  for this process which is more than one order of magnitude faster than  $k_{sq}$  for PE2-ethyl alone. This is likely a result of potential energy barrier associated with steric hindrance of the central platinum and alkyl phosphine chains. There may also be a dependence on the conformation of the two molecules which allows the ligand to be more efficient. Other self-quenching experiments we have performed showed little dependence of the size of the alkyl phosphine chain on the central platinum. Values for the ethyl, butyl, and octyl all share the same order of magnitude. We would therefore expect that the result of the PE2-ethyl experiment to translate to PE2-octyl. It should be noted that PE2-ethyl was substituted in this case because of limited availability of PE2-octyl. It would also be expected that if the platinum were playing a large role in the formation of the triplet excimer that increasing the alkyl phosphine chain would hinder the efficiency of self-quenching which is not the case.

From Scheme 1, a differential equation can also be made to represent the change in excimer concentration,  $[^3E^*]$ , versus time. This equation has been solved previously to yield

$$[^3E^*] = \frac{k_{sq}[M]}{k_e - k_{obs}} [^3M^*]_0 (e^{-k_{obs}t} - e^{-k_et}). \quad (7)$$

This biexponential equation represents the formation and decay of the excimer. However the data is recorded as convolution of monomer and excimer differential absorption. Therefore a combination of equations 6 and 7 is required to fit the transient decay curve.



After combining and substituting  $\Delta A = (\Delta \varepsilon_m [^3M^*] + \Delta \varepsilon_e [^3E^*])l$  and  $\Delta A_0 = \Delta \varepsilon_m [^3M^*]_0 l$ , we have

$$\Delta A = C (e^{-k_{obs}t} - e^{-k_e t}) + \Delta A_0 e^{-k_{obs}t}, \quad (8)$$

where

$$C = \Delta A_0 \frac{k_{sq} [M]}{k_e - k_{obs}} \frac{\Delta \varepsilon_e}{\Delta \varepsilon_m}. \quad (9)$$

Here  $\Delta \varepsilon_m$  has been measured previously through total depletion. Since  $k_{sq}$  and  $k_m$  are already known, that leaves  $k_e$  and  $\Delta \varepsilon_e$  as adjustable parameters. Figure 4 shows the experimental differential absorption data along with equations 2-4 as a function of time superimposed on the raw data. Table 1 shows the values that were determined from those equations for PE2-octyl. We can also solve for the transient absorption spectrum of the triplet excimer by subtracting  $\Delta A$  contributed from the monomer at long times. In Figure 3, at 8.9  $\mu s$  roughly 60% of the differential absorption is a result of the excimer and therefore the monomer can be more easily subtracted. We can calculate the concentration of monomer present at 8.9  $\mu s$  from equation 6 and from there determine its contribution by multiplying through by  $\Delta \varepsilon_m$  at each wavelength. Figure 5 shows the molar extinction coefficient spectrum of the PE2-octyl excimer after subtracting the  $\Delta A$  from the monomer and applying the extinction coefficient measured for the excimer at 600nm.

The order of magnitude for  $k_e$  gives a lifetime of 1.4  $\mu s$  which is considerably shorter than the lifetime of the monomer at 91  $\mu s$  but does correlate to the long decay, 1.2  $\mu s$ , present in the neat sample which was measured previously(8). We speculated earlier that the fast decay of the neat sample could be a result of oxygen quenching,



triplet-triplet annihilation, or self-quenching by triplet excimer formation. The most likely case under the low fluence conditions of laser flash photolysis for the fast decay is a combination of self-quenching and oxygen quenching. Triplet-triplet annihilation will only be a factor under intense laser radiation in which the ground state is depleted.

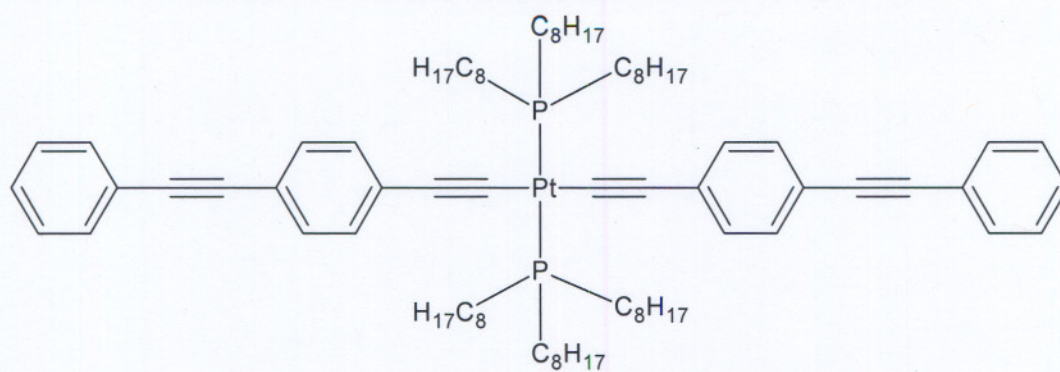
The triplet excimer can be described as a combination of charge transfer and resonance interactions between monomer units(24).

$$\Psi(^3E^*) = c_1\Psi(M^+M^-) + c_2\Psi(M^-M^+) + c_3\Psi(M^*M) + c_4\Psi(MM^*) \quad (10)$$

The experimental observations give insight into the excimer structure. The lack of aggregation effects gives evidence for a repulsive ground state interaction between the monomer units, required for the formation of an excimer. Compared to the monomer triplet state absorption spectrum, the excimer spectrum shows narrowing, vibronic structure, but still has the same peak maximum. This behavior contrasts with that of the naphthalene triplet state excimer, where its triplet state absorption is red-shifted and broadened from that of the monomer(25). This difference suggests the triplet exciton primarily resides on one monomer unit, ruling out strong charge transfer and resonance interactions with the other monomer unit, therefore  $c_3 \gg c_1, c_2$  and  $c_4$ . This behavior is consistent with previous work showing the triplet exciton is confined to one ligand(23). We did not observe any excimer phosphorescence and the excimer decay rate is about 60 times faster than the monomer decay rate. Assuming a small( $\phi < 10^{-3}$ ) excimer emission quantum yield, the rate of non-radiative intersystem crossing is greater than the rate of radiative decay,  $k_{nr}(T_1 \rightarrow S_0) \gg k_r(T_1 \rightarrow S_0)$ . The enhanced quenching rate by the ligand on the platinum complex and the appearance of narrowing and vibronic structure in the excimer triplet absorption spectrum give evidence that steric effects are important in the

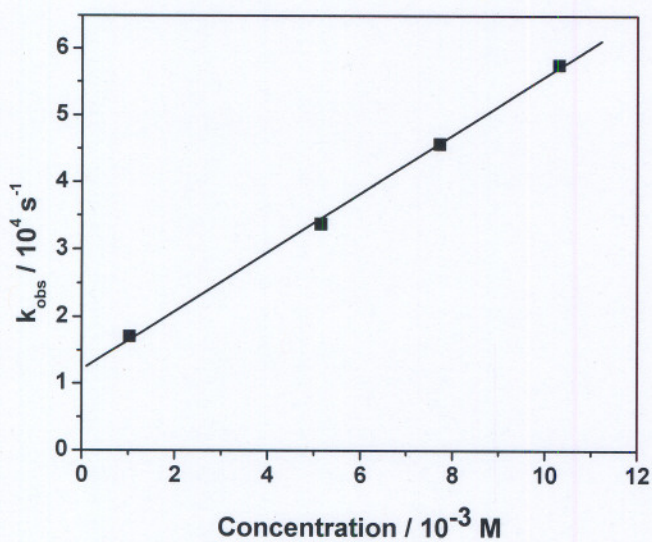


excimer structure. The steric crowding of the octyl groups probably limits the interaction between the ligand units to the outer phenyl acetylene groups. The rate of intersystem crossing results from a combination of Franck-Condon and spin orbit factors. The electronic-vibrational interaction between the frontier orbitals of the two monomer units, combined with the heavy atom effect of the two platinum atoms accounts for the enhanced rate of non-radiative decay to the ground state, but compared to self-quenching in platinum diimine complexes(15), the monomer interactions are weak.

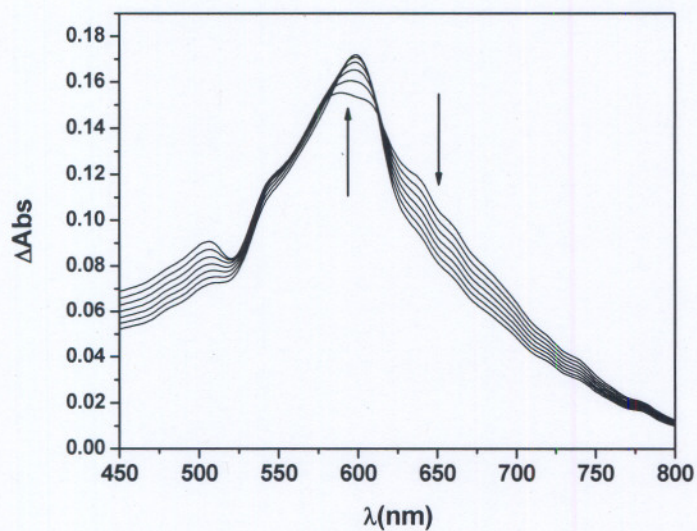


**Figure1:** Chemical structure of PE2-octyl.



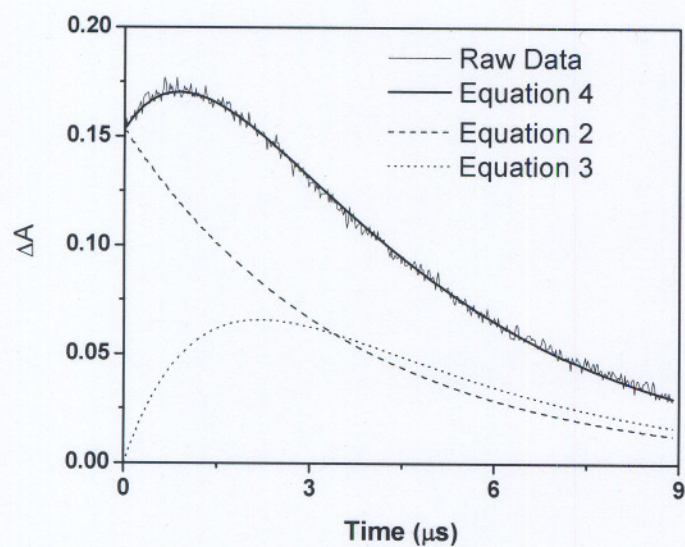


**Figure 2:** Stern-Volmer plot of  $k_{\text{obs}}$  vs. concentration for PE2-octyl in deoxygenated benzene. Laser excitation wavelength was 397, 400, 408, and 411 nm starting from lowest concentration to highest.

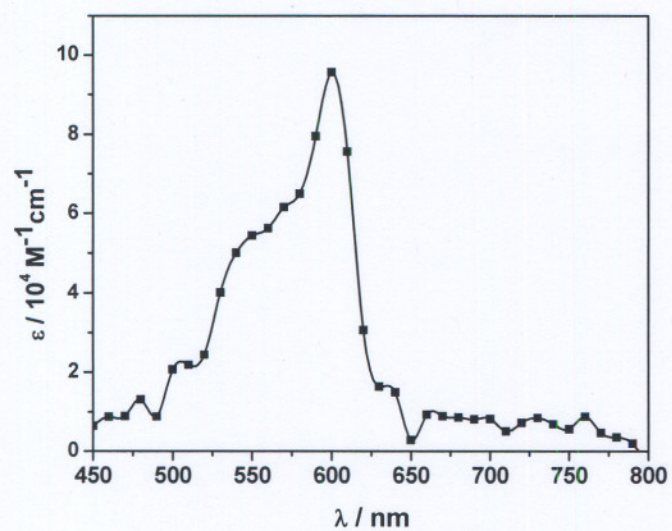


**Figure 3:** Transient absorption spectra of 57mM PE2-octyl in deoxygenated benzene after 476nm laser excitation at different times. At 600nm the time increases from zero, 150, 300, 450, 600, 750, and 900ns in the direction of the arrow.





**Figure 4:** 600nm transient decay of 57mM PE2-octyl in deoxygenated benzene following laser excitation of 476nm.



**Figure 5:** Molar extinction coefficient for PE2-octyl excimer in deoxygenated benzene.



	$k_e / 10^5 \text{ s}^{-1}$	$k_{sq} / 10^6 \text{ M}^{-1} \text{ s}^{-1}$	$k_m / 10^4 \text{ s}^{-1}$	$\Delta\epsilon_{m(600\text{nm})} / \text{M}^{-1} \text{ cm}^{-1}$	$\Delta\epsilon_{c(600\text{nm})} / \text{M}^{-1} \text{ cm}^{-1}$
PE2-octyl	$6.94 \pm 0.05$	$4.7 \pm 0.3$	$1.1 \pm 0.2$	46740	95680

**Table 1:** Kinetic rate constants and differential extinction coefficients for PE2-octyl.



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